

clear solution resulted from which the brucine salt precipitated when the side of the beaker was rubbed with a stirring rod. The mixture was cooled and filtered, yielding 12.8 g. of salt which gave  $[\alpha]_D -37^\circ$ . On concentrating the filtrate, 10 g. of salt of  $[\alpha]_D +12^\circ$  was obtained. The first fraction was recrystallized from 200 cc. of absolute alcohol to constant rotation. The more soluble fraction was recrystallized from ethyl acetate.

*l*-Salt.—0.1137 g. made up to 15 cc. with chloroform at  $20^\circ$  gave  $\alpha_D -0.68^\circ$ ;  $l = 2$ ;  $[\alpha]_D^{20} -44.9^\circ$ ; m. p. 231–232° (dec.).

*Anal.* Calcd. for  $C_{37}H_{39}O_8N_3$  (monobrucine salt): C, 67.96; H, 6.0. Found: C, 67.74; H, 6.1.

*d*-Salt.—0.1551 g. made up to 15 cc. with chloroform at  $20^\circ$  gave  $\alpha_D +0.28^\circ$ ;  $l = 2$ ;  $[\alpha]_D^{20} +13.5^\circ$ ; m. p. 175–180° (dec.).

*Anal.* Calcd. for  $C_{37}H_{39}O_8N_3$ : C, 67.96; H, 6.0. Found: C, 67.71; H, 6.1.

*d*- and *l*-N-2-Carboxyphenyl-2,5-dimethyl-3-carboxypyrroles.—The salts were decomposed by shaking in a separatory funnel with dilute hydrochloric acid and ether. The acid went into the ether layer and was obtained by evaporating to dryness. The acids were crystallized from ethyl acetate to constant rotation.

*l*-Acid.—0.1349 g. made up to 15 cc. with absolute alcohol at  $20^\circ$  gave  $\alpha_D -0.49^\circ$ ;  $l = 2$ ;  $[\alpha]_D^{20} -27.2^\circ$ ; m. p. 203–204°.

*d*-Acid.—0.1753 g. made up to 15 cc. with absolute alcohol at  $20^\circ$  gave  $\alpha_D +0.63^\circ$ ;  $l = 2$ ;  $[\alpha]_D^{20} +27.0^\circ$ ; m. p. 202–204°.

**Racemization Experiments.**—About 0.3 g. of *l*-compound in 50 cc. of absolute alcohol was boiled for eight hours. No change in initial rotation took place. In boiling glacial acetic acid, the rotation dropped to nearly zero in one hour but there was obviously decomposition occurring which probably accounted for this. Only a gram could be recovered from the heated solution.

A solution of 0.2107 g. of *l*-acid in 25 cc. of 0.1 *N* sodium hydroxide gave an initial rotation of  $\alpha_D -0.39^\circ$  ( $[\alpha]_D^{20} -23.1$ ). After eighteen hours' standing at room temperature, no change occurred. Upon boiling for twenty-four hours, the rotations were as follows: 1 hr.,  $\alpha_D -0.39^\circ$ ; 4 hrs.,  $\alpha_D -0.31^\circ$ ; 8 hrs.,  $\alpha_D -0.26^\circ$ ; 24 hrs.,  $\alpha_D -0.03^\circ$ . Upon acidification racemic acid was obtained, m. p. 224–225°.

### Summary

The preparation and resolution of N-2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole has been described.

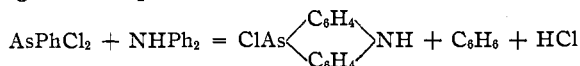
URBANA, ILLINOIS

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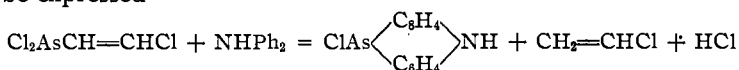
### NOTES

**The Reaction between Dichloro-arsines and Secondary Aromatic Amines.**—Lewis and Stiegler [THIS JOURNAL, 52, 4164 (1930)] appear to have overlooked work already published on this subject.

Burton and Gibson [J. Chem. Soc., 464 (1926)] having shown that the reaction between phenyldichloro-arsine and diphenylamine did not yield 10-phenyl-5,10-dihydrophenarsazine but 10-chloro-5,10-dihydrophenarsazine according to the equation



were led to compare the analogous reaction using  $\beta$ -chlorovinylchloro-arsine as described by Lewis and Stiegler [THIS JOURNAL, 47, 2546 (1925)]. They found (*loc. cit.*, p. 466) that not only is 10-chloro-5,10-dihydrophenarsazine and not "6-chlorovinylphenarsazine" formed by the action of  $\beta$ -chlorovinylchloro-arsine on diphenylamine, but, by proving the production of vinyl chloride in the reaction, showed that the course of the latter may be expressed



Burton and Gibson also proved that the reaction between phenyldichloro-arsine and other substituted diphenylamines and of  $\beta$ -chlorovinylchloro-arsine and phenyl- $\alpha$ -naphthylamine proceeds analogously. These results have since then been fully verified by Seide and Gorski [*Ber.*, 62, 2186 (1929)]. Scherlin and Epstein [*Ber.*, 61, 1823 (1928)] have also shown that the reaction between  $\beta$ -chloro-ethylchloro-arsine and diphenylamine yields 10-chloro-5,10-dihydrophenarsazine, the reaction being quite similar.

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C. S. GIBSON

**Phenylmagnesium Fluoride.**—The relative reactivities of RX compounds with magnesium in ether is in the order  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ . Actually, only one  $\text{RMgF}$  compound (*n*-amylmagnesium fluoride) has been prepared, and this synthesis was effected by unusually extensive refluxing with a large quantity of iodine.

In connection with studies concerned with improved catalysts for the formation of organomagnesium halides, it was observed that none of the highly active catalysts induced a reaction between fluorobenzene and magnesium in ether. There has been described recently a satisfactory method for the preparation of phenylmagnesium chloride in the absence of a solvent, and this method is distinctly superior to the very slow formation of this compound when ether is used with varying quantities of iodine and with the magnesium-copper alloy.<sup>1</sup> In this study involving no solvent and a sealed tube it was shown that when fluorobenzene was heated with magnesium at 300° for about 200 hours, a small quantity of diphenyl formed. The formation of diphenyl is almost certain evidence for the intermediate formation of phenylmagnesium fluoride,<sup>2</sup> and the statement was made that this Grignard reagent would probably be prepared by heating at a lower (as yet undetermined) temperature for a longer time.

<sup>1</sup> Gilman and St. John, *Rec. trav. chim.*, 49, 717-723 (1930).

<sup>2</sup> Gilman and Brown, THIS JOURNAL, 52, 5045 (1930).

It now appears, in strict accordance with our knowledge of the very deliberate rate of reaction of chlorobenzene and magnesium in ether,<sup>1</sup> that even the most refractory RX compound will probably react with magnesium in ether if sufficient time be permitted for such a reaction. This finds support in some studies made in sealed, small test-tubes wherein it has been shown that fluorobenzene undergoes reaction with the activated magnesium-copper alloy in ether after being allowed to stand at room temperatures for eighteen months, and that phenylmagnesium fluoride is formed. Individual tubes opened at intervals of one month showed no positive color test at the end of six months. Reaction, therefore, had set in some time between six and eighteen months. Quite probably a compound like *p*-difluorobenzene will form *p*-fluorophenylmagnesium fluoride more readily, because *p*-dichlorobenzene reacts more readily than chlorobenzene.

It is altogether reasonable to expect that a distinctly shorter time will be required for the formation of phenylmagnesium fluoride when the proper temperature range in sealed-tube experiments is determined or when superior catalysts are discovered. At present, however, if one desires a *pure* RMgX compound from a highly inert RX compound, it is merely necessary to enclose the reactants in a container to exclude the atmosphere and moisture and wait for the reaction to run its course. The compensations for such devastating delays are that the RMgX compound will almost certainly be of a high order of purity and will be formed in a high yield because side reactions are drastically reduced with the use of relatively inert RX compounds. The difficulties in most cases are more apparent than real because of the ready accessibility of the related RBr and RI compounds. In our case we needed phenylmagnesium fluoride in studies on the relative reactivities of some organometallic compounds.

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LLOYD L. HECK

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**A New Compound of Benzaldehyde and Anthrahydroquinone.**—During an investigation on the autoxidation of anthrahydroquinone in benzaldehyde solution,<sup>1</sup> it was found that such a solution (oxygen being excluded), when containing a trace of hydrochloric acid, gave on standing in the dark at room temperature for twelve to seventy-two hours a new compound in good yield. The presence of benzoic acid appeared to favor larger yields. No reaction occurred: (1) in the absence of hydrochloric acid; (2) with anthrone substituted for anthrahydroquinone; or (3) between anthrahydroquinone and either benzoic acid or benzoin in acetone solutions.

<sup>1</sup> Bäckström and Beatty, to be published.

Since free anthrahydroquinone is awkward to handle on account of its oxidizability, a more convenient preparation of the compound is as follows. Take 250 cc. of commercial benzaldehyde, 10 g. of anthraquinone, 10 g. of benzoic acid, 1 cc. of hydrochloric acid and 20 cc. of ethyl alcohol (to favor the photo-reduction of the anthraquinone):<sup>2</sup> seal the container to exclude oxygen and expose the mixture to sunlight or other illumination until the anthraquinone has dissolved. Steam distil the solution to remove aldehyde, etc., then treat the remaining tar with enough alcohol and ether to dissolve the resinous matter, leaving a dry, crystalline residue. Dissolve this in hot alcohol and add two volumes of filtered sodium hydrosulfite solution (100 g. of hydrosulfite and 100 g. of sodium hydroxide per liter of water) and two volumes of water: the anthraquinone remains in solution, and the compound may be filtered off and recrystallized from alcohol or acetone. The yield is only about 10% of the anthraquinone taken.

The compound is slightly soluble in ether, acetone and 95% alcohol (0.6 g. per 100 cc. at the boiling point), and readily soluble in hydrocarbons; the solutions are not fluorescent. It dissolves in concentrated sulfuric acid with a red color turning brown. Acetone and alcohol solutions give identical crystals—large, colorless, hexagonal tablets—melting at 211–212° (corr.) with decomposition and sublimation of anthraquinone.

Aqueous alkali is without effect on the compound; alcoholic alkali causes a very slow hydrolysis; with alcoholic hydrochloric acid the action is faster (20 mg. per hour per 25 cc.). The products of hydrolysis are benzaldehyde, qualitatively detected by its odor, and anthrahydroquinone, distinguished by its characteristic fluorescence which disappears on shaking with air.

## ANALYSES

Calculated values are for $C_{14}H_8(OH)_2 + 2C_6H_5CHO - H_2O = C_{24}H_{24}O_3$					
	C, %	H, %	Mol. wt.*	Anthraquinone, % <sup>b</sup>	Benzaldehyde, % <sup>c</sup>
Found	82.91	5.00	416 ± 20	51.8 ± 1.5	52.7 ± 1.0
	83.03	4.97	405	50.2	
				50.2	
Calcd.	82.94	4.99	404.3	51.49	52.48

\* By the method of Menzies and Wright, *THIS JOURNAL*, **43**, 2309 (1921). <sup>b</sup> By spectrophotometric analysis (Ref. 1) of a solution of the hydrolyzed material. <sup>c</sup> By precipitation, from a similar solution, of the *p*-nitro-phenylhydrazone (the melting points of the precipitated and synthetic hydrazones were identical, 187.5–188° (uncorr.)).

The properties and analyses of this substance indicate a structure of the quinone and of the acetal type, containing no free hydroxyl or acyl groups, and probably derived by condensation of two molecules of benz-

<sup>2</sup> Compare, Meyer and Eckert, *Monatsh.*, **39**, 249 (1918).

aldehyde with one of oxanthrone (the tautomeric form of anthrahydroquinone).

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HAROLD A. BEATTY

**Note on the Interaction of Tertiary Butyl Chloride and Naphthalene.**—Wegscheider<sup>1</sup> had studied the reaction between isobutyl chloride and naphthalene in the presence of anhydrous aluminum chloride and had obtained isobutylnaphthalene boiling at 280°. The so-called isobutylnaphthalene was probably  $\alpha$ -tertiary butylnaphthalene, b. p. 278–287°, which was later prepared from  $\alpha$ -naphthylmagnesium bromide and *tert.*-butyl bromide by Späth.<sup>2</sup>

Besides the liquid butylnaphthalene, Wegscheider had also obtained a small amount of two solid substances, one crystallizing in fine, white needles of m. p. 80° and the other forming white leaflets or prisms of m. p. 146–147°. Wegscheider thought that probably the lower-melting compound was  $\alpha,\beta$ -dinaphthyl and the substance of m. p. 146–147° was  $\alpha,\alpha$ -dinaphthyl (m. p. 154°), being somewhat impure and therefore of depressed melting point.

The writer tried to prepare *tert.*-butylnaphthalene from one mole of *tert.*-butyl chloride and one mole of naphthalene using a small amount (about 1% of the combined weight) of aluminum chloride as catalyst and finally heating the mixture just above its melting point until no hydrogen chloride came off. A liquid mono-*tert.*-butylnaphthalene of b. p. 280° never was formed; on distilling the reaction product, about half a mole of naphthalene was recovered and a fraction boiling over 300° was obtained. On changing the proportions of the starting materials to two moles of *tert.*-butyl chloride and one mole of naphthalene, practically all of the naphthalene was converted into two isomeric di-*tert.*-butylnaphthalenes which could be separated by fractional crystallization from methanol or ethanol. The one as the main product is quite soluble in these alcohols and forms fine, white needles of a salol-like odor. The substance melts at 82–83° and boils at 319°.

*Anal.* Subs., 0.1200, 0.1285; CO<sub>2</sub>, 0.3960, 0.4230; H<sub>2</sub>O, 0.1075, 0.1139. Calcd. for C<sub>18</sub>H<sub>24</sub>: C, 89.93; H, 10.07. Found: C, 90.03, 89.91; H, 10.03, 9.92.

The other di-*tert.*-butylnaphthalene, melting at 145–146° and boiling at 320°, crystallizes in white prisms and is not easily soluble in alcohol.

*Anal.* Subs., 0.1271, 0.1205; CO<sub>2</sub>, 0.4185, 0.3963; H<sub>2</sub>O, 0.1147, 0.1086. Calcd. for C<sub>18</sub>H<sub>24</sub>: C, 89.93; H, 10.07. Found: C, 89.93, 89.72; H, 10.10, 10.09.

<sup>1</sup> Wegscheider, *Monatsh.*, **5**, 238 (1884).

<sup>2</sup> Späth, *ibid.*, **34**, 2013 (1913).

An attempt was made to establish the position of the *tert.*-butyl groups in the naphthalene ring by means of boiling the di-*tert.*-butylnaphthalenes with dilute nitric acid, but no oxidation to the naphthalene-dicarboxylic acids took place.

Very probably Wegscheider had already obtained these two isomeric di-*tert.*-butylnaphthalenes but his belief that his compounds of m. p. 80° and 146–147° were  $\alpha,\beta$ -dinaphthyl and  $\alpha,\alpha$ -dinaphthyl was erroneous.

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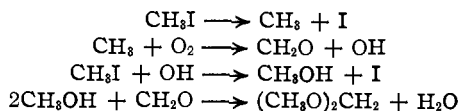
## COMMUNICATIONS TO THE EDITOR

### PHOTOCHEMICAL REACTIONS OF GASEOUS METHYL IODIDE

Sir:

In a recent communication to *Nature*, Iredale<sup>1</sup> has discussed the action of light upon gaseous methyl iodide. From a study of the short wave limit of the absorption spectrum, he calculates the energy of the C–H bond to be 65 Cal. and suggests, with Herzberg and Scheibe,<sup>2</sup> that the initial process is the dissociation of methyl iodide into CH<sub>3</sub> and I, since the absorption is continuous. Studies of the photochemical decomposition and oxidation of gaseous methyl iodide in progress in this Laboratory for some time past lend additional support to the idea that CH<sub>3</sub> and I are the initial products. The reaction behaves as though the process were actually that of the oxidation of free methyl groups. Formaldehyde, paraformaldehyde and methylal seem to be the products, while the iodine originally present in the methyl iodide can in all cases be recovered as free iodine.

A possible mechanism for the process is



Kinetic measurements are being made to determine the actual mechanism.

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<sup>1</sup> Iredale, *Nature*, 604, Oct. (1930).

<sup>2</sup> Herzberg and Scheibe, *Trans. Faraday Soc.*, 25, 716 (1929).